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DEVELOPMENT OF HYDROCARBON ANALYSES  
AS A MEANS OF DETECTING LIFE IN SPACE

Contract No. NASw-508

OTS PRICE	
XEROX	\$ <u>1/10 ph</u>
MICROFILM	\$ _____

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## SUMMARY

Gas chromatograms of alkanes obtained with Apiezon L coated capillary columns apparently provide a means of "fingerprinting" mixtures of saturated hydrocarbons. Alkanes from bat guano and from a 60 million year old sediment, both, contain higher concentrations of even- than of odd-carbon number n-paraffins in the  $C_{11}$  to  $C_{20}$  range and higher concentrations of odd- than of even-carbon number n-paraffins in the  $C_{23}$  to  $C_{31}$  range. Fischer-Tropsch saturated hydrocarbons on the other hand show a systematic increase followed by a systematic decrease in concentrations of homologous alkanes. These concentrational changes can be explained by the loss of volatile components from an abiotic product in which the reaction equilibria led to a decrease in concentration of homologous hydrocarbons with increasing carbon number. Nonsystematic fluctuations in the concentration versus carbon number plots of homologous alkanes appear to be characteristic of biological alkanes of low as well as of high molecular weights. Components of the benzene extract of the Orgueil meteorite vary nonsystematically in concentration with changing carbon number.

## INTRODUCTION

Efforts during the second quarter of NASw-508 contract have been directed toward:

1. The development of gas chromatographic methods for the characterization and identification of alkanes.
2. The modification of the Consolidated 21-103C mass spectrometer.
3. The fingerprinting of alkanes from biological, sedimental, and abiotic sources.
4. A determination of the stability of the "fingerprints" of biological alkanes incorporated in sediments.

## STATUS OF RESEARCH PROJECT

Installation of the Barber-Colman Model 10 gas chromatograph has been completed. Repeated attempts to repair a temperature programmer, which was damaged in shipment, have been unsuccessful and the supplier will replace the damaged unit.

Methods of "fingerprinting" alkane mixtures have been developed. Satisfactory characterizations of alkanes in the  $C_{10}$  to  $C_{28}$  range can be obtained, but  $C_{28}$  to  $C_{33}$  hydrocarbons are retained and in part are randomly released from the Apiezon L coated capillary columns. Reference chromatograms of alkanes from butter, oysters, bat guano, cow manure, Recent marine sediments, ancient sediments, crude oil, and a Fischer-Tropsch product are on file. These data clearly indicate that biological patterns may persist in sedimental alkanes for at least 60 million years.

A variety of substrates have been prepared for the analytical and preparatory columns. Florsal, a hydrogenated pine resin, on Chromsorb "W" was too volatile to use in the separation of  $C_{20}$  and larger alkanes. Separations have been obtained on SE 30 silicone and Apiezon L on Analabs and Chromsorb "W" supports in analytical and preparatory size columns, but the problem of maintaining a constant sample splitting ratio for the preparatory column has not been solved.

Modifications of the Consolidated 21-103C mass spectrometer are nearly complete, and the modified unit should be ready for testing within two weeks.

One hundred pounds of bat guano and 150 pounds of cow manure have been extracted with benzene. Liquid phase chromatographic fractionation<sup>(1)</sup> of the bat guano and a portion of the cow manure extract yielded 5.7 grams and 1.5 grams of biological alkanes respectively. n-Paraffins isolated in the urea adducted fraction of the cow manure alkanes are being used as references for the location of the n-paraffin peaks in the chromatograms of other saturated hydrocarbon mixtures.

A 5 gram portion of the alkanes isolated from a Pleistocene crude oil have been<sup>(2)</sup> fractionated on an alumina column at a gel to sample ratio of 10,000 to 1. This fractionation separates alkanes by molecular weight and type, and the alumina fractions of the crude oil alkanes are being employed in the development of techniques for the isolation and identification of biological alkanes.

## DISCUSSION

The identification of living things or the remnants of former life may be easier to accomplish than to explain. Most inanimate things can be precisely described by equations; whereas plants and animals have a difficultly definable order that greatly exceeds the order found in inorganic materials.

Natural laws do not favor highly ordered systems. Living things exist only as long as complex organic molecules, working in concert, acquire and direct energy to the maintenance of the living state. When an organism dies, most of the order associated with it is lost. Nonetheless, legible records of prehistoric life and ancient civilizations have been found in the stable remnants and artefacts of life that can resist the erosion of time.

Although most studies of prehistoric organisms have been dependent on fossilized cellular<sup>(3)</sup> and skeletal remains, recent investigations and theoretical considerations<sup>(3)</sup> indicate that certain alkanes may be more ubiquitous and less altered remnants of life than are fossils. Alkanes appear in the unsaponifiable portion of the lipid fractions of plants, animals, and sediments. Distributional and structural<sup>(4,5)</sup> similarities between biological and sedimental alkanes have been reported<sup>(4,5)</sup>, furthermore, the first four  $C_{14}$  or larger branched chained paraffins identified in petroleum are saturated norisoprenoids and isoprenoids that were previously identified in living things<sup>(6,7,8,9,10)</sup>. Alkanes are the most stable of the known biological substances.

Data presented in Figures 1 through 4 show the distributions of n-paraffins in cow manure and of the alkanes from bat guano, ancient sediments and a Fischer-Tropsch product. After the carbon numbers of the cow manure n-paraffins were established by reference compounds, these n-paraffins were used to determine the carbon number and position of the n-paraffin peaks in the chromatograms of other mixtures of alkanes. Noteworthy, in Figures 2 and 3, are the periodicities of the n-paraffin concentrations in the  $C_{11}$  to  $C_{20}$  and in the  $C_{23}$  to  $C_{30}$  ranges. In the lower carbon number range the even-carbon number n-paraffins are most abundant, whereas in the higher carbon number range the odd-carbon homologs are most abundant. Since the sedimental hydrocarbons shown in Figure 3 are approximately 60 million years old, the data in Figures 2 and 3 indicate that biological hydrocarbons can retain their distinctive distributions in some sediments for at least 60 million years. Previously, spectrometric and spectroscopic analyses have been cited as evidence that some biological alkanes maintain their structural integrity for hundreds of millions of years<sup>(4)</sup>. Changes in the concentrations of the Fischer-Tropsch alkanes in Figure 4 follow a simple pattern. Their concentrations increase at low carbon number because some of the volatile alkanes were lost when the sample was recovered from the solvents used in isolating these alkanes from other Fischer-Tropsch products. The systematic decrease in the high molecular alkanes in Figure 4 indicate that yields of alkanes decrease with carbon number in this abiotic synthesis<sup>(11)</sup>.

Figure 5 presents a chromatogram of a benzene extract of the Orgueil meteorite. This chromatogram was furnished by Professor D. J. Hennessy of Fordham University, and it was obtained on an analytical rather than a capillary column. Although a direct comparison between the data in Figure 5 and in Figures 1-4 is not permitted, it is of interest that the peak heights in the chromatogram of the meteoritic extract vary nonsystematically.

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FIGURE 1

n-PARAFFINS FROM COW MANURE  
(UREA ADDUCT OF BIOLOGICAL ALKANES)  
APIEZON L - CAPILLARY

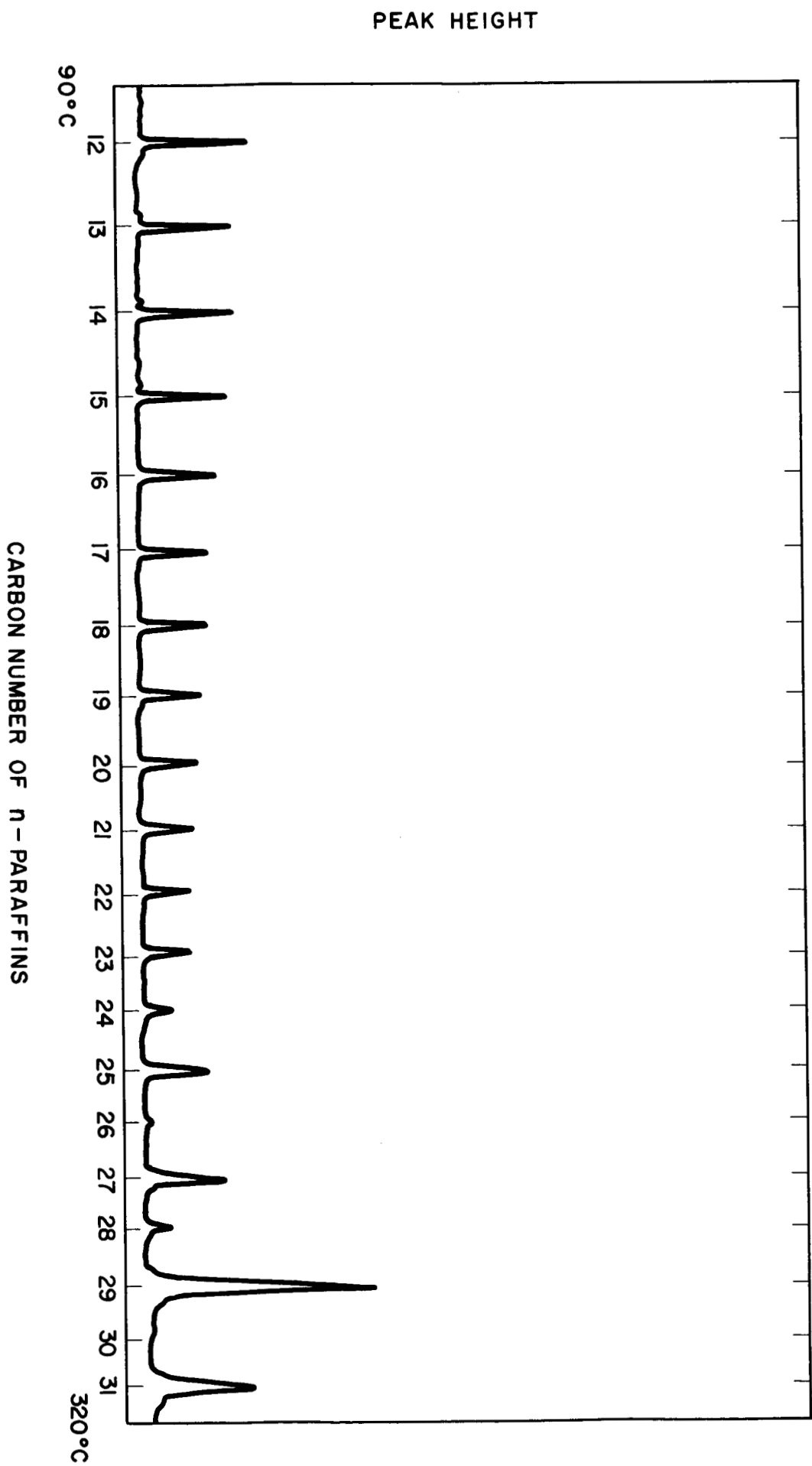


FIGURE 2

GAS CHROMATOGRAM  
ALKANES FROM BAT GUANO  
AGE  $\approx 5 \times 10^3$  YEARS  
APIEZON L - CAPILLARY

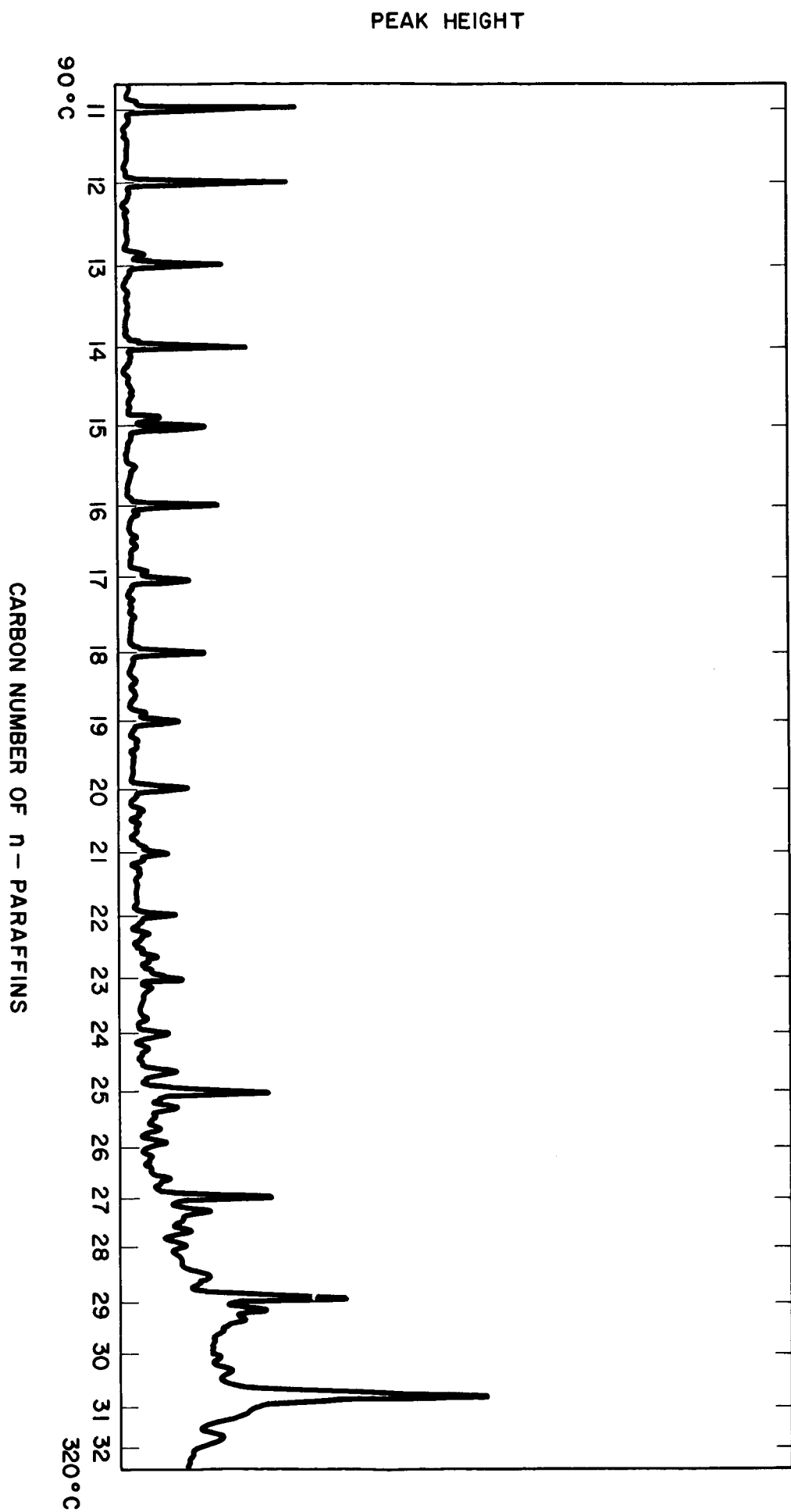


FIGURE 3  
GAS CHROMATOGRAM  
ALKANES FROM EOCENE SEDIMENTS  
AGE  $\approx 6 \times 10^7$  YEARS  
APIEZON L - CAPILLARY

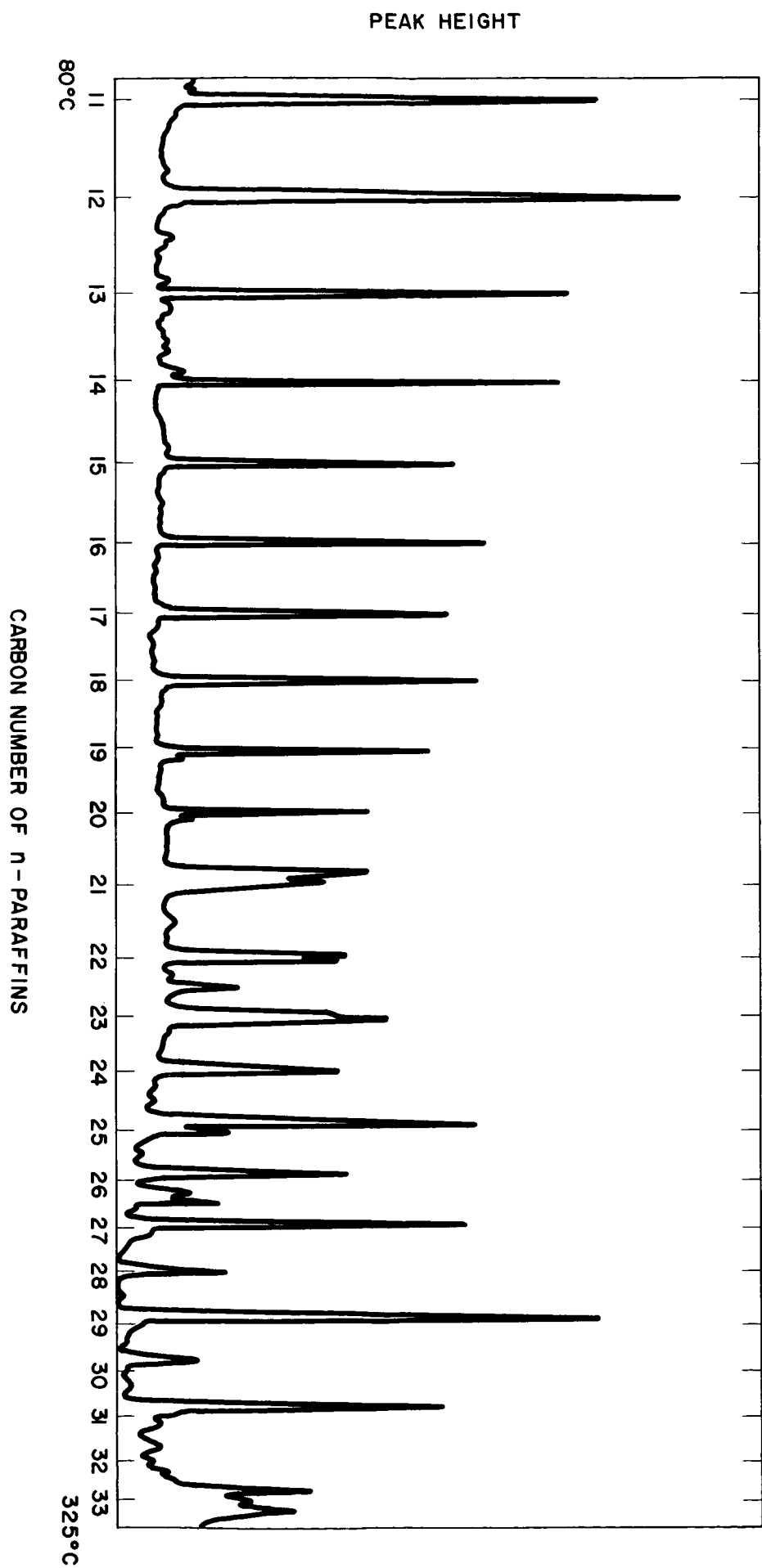


FIGURE 4

GAS CHROMATOGRAM  
FISHER-TROPSCH (ABIOTIC) ALKANES  
APIEZON L - CAPILLARY

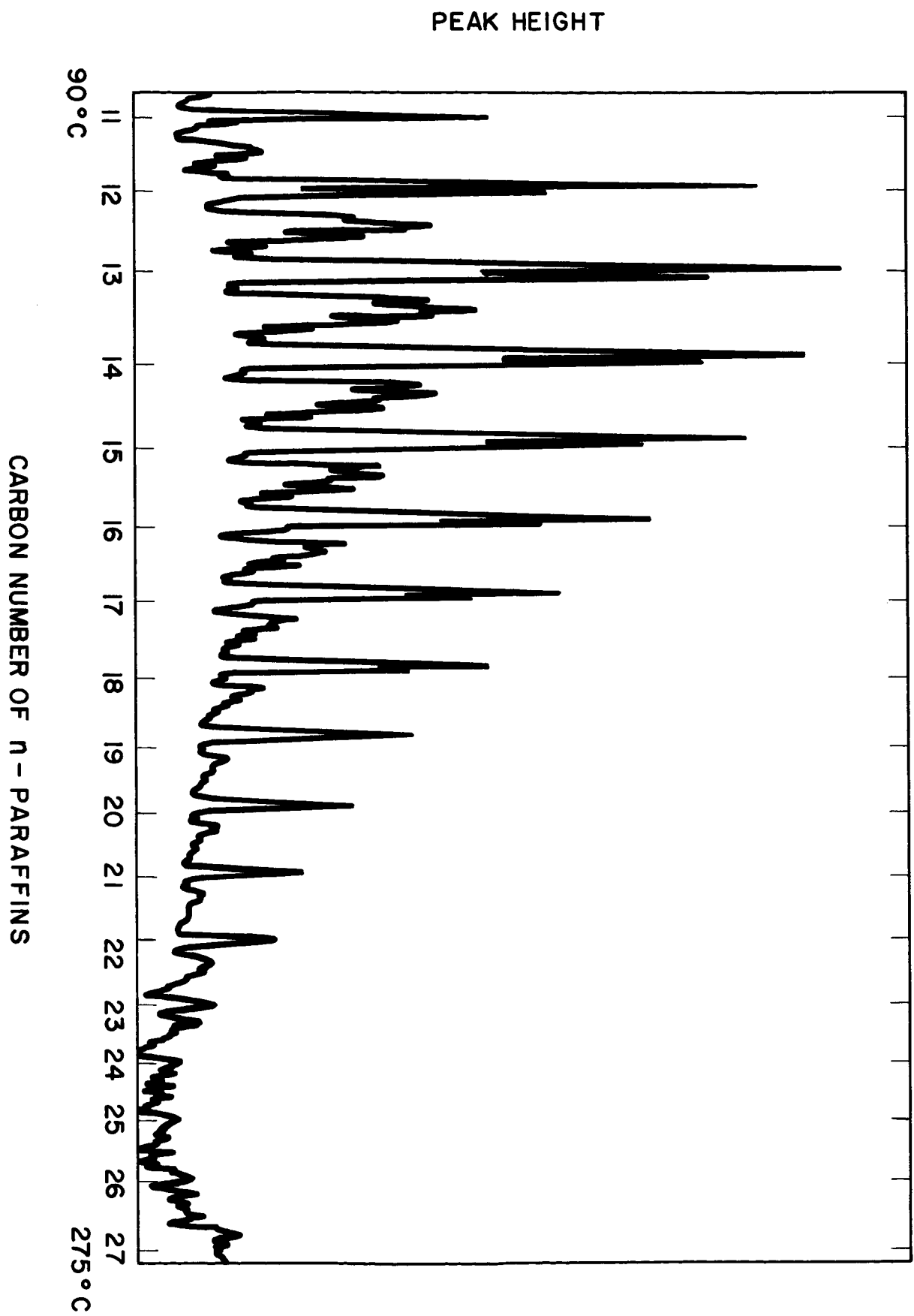


FIGURE 5

GAS CHROMATOGRAM  
BENZENE EXTRACT OF ORGUEIL METEORITE  
APIEZON L - ANALYTICAL COLUMN

